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(19)

(54) POLYMERIC COMPOUNDS AND PROCESSES FOR THEIR PREPARATION

(71) We, I.W.S. NOMINEE COMPANY LIMITED, a British Company, of Wool House, Carlton Gardens, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to novel polymeric compounds containing thiosulphuric acid or thiosulphate groups, or their cured products, which have useful applications to textile fibres and to living human hair. The application of these and other compounds containing thiosulphuric acid or salt groups is claimed in Application No. 57313/71 (Serial No. 1,423,341).

The invention provides novel polymeric compounds containing at least one poly (oxyalkylene) chain and substantially two or more thiosulphuric acid or thiosulphate groups each such group being bound through an organic acyl group to a terminating oxygen atom of a poly (oxyalkylene) chain. The thiosulphuric acid or thiosulphate group may conveniently be referred to as Bunte salt group. It will be understood that what are referred to here are molecular species containing at least two Bunte salt groups per molecule. It should be appreciated that an insoluble cured product may be obtained from such species when present in a commercial mixed product having in bulk a statistical Bunte salt group content of less than two.

These Bunte salt compounds are water soluble and may have surface active properties and can conveniently be prepared and used in the form of their sodium or potassium salts. They can be cured to novel water-insoluble condensation products and can be used in textile finishing. For example they may be employed for pigment-dyeing and printing of fibrous materials such as wool fabrics, polyester fabrics, cellulosic fabrics and paper. When applied as textile finishing agents to cotton, rayon, polyamide or polyester fibres or fabrics they can impart shape stabilisation thereto. In addition they may also act as antistatic agents. When applied to keratinous fabrics they can impart shrink resist properties and additionally certain compounds can be used for flat setting and permanent creasing of the fabric. They may also be used for the treatment of living human hair. Because of their surface active properties they can be incorporated into shampoos and can impart to the hair an attractive handle. In addition they may be employed for the permanent waving or setting of hair.

A preferred group of compounds according to the invention comprises:

(a) a radical of a polyhydric alcohol;
(b) bound to this radical at least two poly (oxyalkylene) chains; and
(c) at least two Bunte Salt groups each bound through an alkylenecarbonyl group group to a chain terminating oxygen atom.

Compounds of especial interest contain three polyoxyalkylene chains and up to three Bunte Salt groups per molecule and have molecular weights in the range 500—10,000, especially 1,500—5,000. The linking groups may be the same or different in different poly (oxyalkylene) chains, and may be, for example, alkylene chains which may contain from 1 to 6 carbon atoms and may be unsubstituted or substituted with, for example, one or more hydroxyl groups. The linking groups may also be divalent acyl radicals of carboxylic acids. The compounds of the invention may also contain free hydroxyl or thiol groups or polyoxyalkylene chains linked together by thioether or disulphide bridges.

Compounds according to the invention may be represented by the general formula:

$$[R]\begin{matrix}[(\text{O-alkylene})_m\,OH]_q\\ [(\text{O-alkylene})_m\,OX\,SSO_3Y]_p\end{matrix} \qquad I$$

or by the general formula

$$YO_3SSX—(\text{O-alkylene})_m—OXSSO_3Y \qquad II$$

wherein

p is an integer from 2 to 6;

q is such that (p+q) is from 2 to 6;

m is an integer of value at least 2 (most usually from 5 to 25) and may have different values in each of the p and q chains;

R represents a radical formed by removal of the hydroxyl groups from an aliphatic polyhydric alcohol containing at least two carbon atoms; each 'alkylene' group contains a chain of at least 2 and at most 6 carbon atoms between consecutive oxygen atoms;

X represents $—CO(CH_2)_n—$ where n is an integer from 1 to 5;

Y represents a hydrogen atom or a salt forming ion or group.

The preferred compounds are of the general formula

$$R_1\ [(\text{O-alkylene})_m\,O\,X\,SSO_3\,Y]_{p1} \qquad III$$

wherein m, X and Y and 'alkylene' are as defined in formula I, R_1 represents a radical derived from an aliphatic polyhydric alcohol containing from 3 to 6 carbon atoms and from 3 to 6 hydroxyl groups and p_1 is an integer from 3 to 6.

The compounds may also contain disulphide linkages between polyoxyalkylene chains. Where the linkage is between chains attached to different groups R_1 the compounds may be of the formula IV.

$$[R_1]\begin{matrix}[(\text{O-alkylene})_m—OX—S—S—XO—(\text{alkylene-O})_m]\\ [(\text{O-alkylene})_m OXSSO_3Y]_{p2}\ _{p2}[YO_3SSXO)\text{alkylene-O})_m]\end{matrix}[R_1] \qquad IV$$

wherein R_1 has the meaning given in formula III, 'alkylene', m, X and Y have the meaning given in formula I and p_2 represents an integer from 2 to 5. The compounds may also contain disulphide linkages between polyoxyalkylene chains bound to the same group R_1 and in this case may be of the general formula V.

$$\left[R_1\right]\begin{matrix}(\text{O-alkylene})_m\,O\,X\,S\\ \quad\vdots\\ (\text{O-alkylene})_m\,O\,X\,S\\ [(\text{O-alkylene})_m\,O\,X\,SSO_3Y]_{p3}\end{matrix} \qquad V$$

wherein R_1 has the meaning given in formula III, m and 'alkylene' have the same meanings as in formula I and p_3 represents an integer from 1 to 4.

The group R represents a radical formed by notional removal of the hydroxyl groups from an aliphatic polyhydric alcohol. Suitable radicals are, for example, those derived from ethylene glycol, propylene glycol, cyclohexane 1,4-diol, 1,1,1-trimethylolethane, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, pentaerythritol and sucrose. The group R may also comprise a hydroxy terminated adduct of one or more alkylene oxides with ammonia or an amine, examples of such compounds being the propylene oxide adducts of ammonia, ethylenediamine, or triethanolamine. Preferably R is derived from an alcohol containing three hydroxyl groups, and the preferred radical is derived from glycerol.

The alkylene groups may be C_2H_4, or C_3H_6 or C_4H_8 radicals. Compounds containing C_3H_6 and/or C_4H_8 radicals are hydrophobic and the Bunte Salt compounds derived therefrom act as surface active agents. The compounds may, for example, contain mixture of C_2H_4 and C_3H_6 derived groups and may be random or block copolymers. The surface tension properties may be adjusted by selection of the

ratio of C_2H_4 to C_3H_6 radicals. For example a suitable triol may be formed as a block copolymer by condensing glycerol with propylene oxide and "tipping" the resulting triol with ethylene oxide.

Condensation products of glycerol and ethylene oxide and/or propylene oxide are available commercially, for example, those sold under the Trade Marks Polyurax (B.P. Chemicals), Caradol (Shell Chemical Co) and Propylan (Lancro Chemicals Ltd.).

The group X may be substituted or unsubstituted.

Compounds of especial interest have molecular weights in the range 1,500—5,000 and are of the formula

$$\begin{array}{l} CH_2\ (OC_3H_6)_mOCO\ CH_2\ SSO_3H \\ | \\ CH\ (OC_3H_6)_mOCO\ CH_2\ SSO_3H \\ | \\ CH_2\ (OC_3H_6)_mOCO\ CH_2\ SSO_3H \end{array} \qquad \text{VI}$$

wherein m has the same meaning as in formula I. Water soluble salts, for example the alkali metal (especially sodium), ammonium or amine salts may also be used.

Preparative Methods

Polymeric compounds according to the invention may be prepared by esterifying an alcohol containing at least one poly (oxyalkylene) chain and at least two terminal hydroxyl groups with a halogen substituted carboxylic acid or functional derivative thereof and reacting the resulting halogeno-ester with a water soluble thiosulphate. If the alcohol is of the general formula

$$[R]\quad[(\text{O-alkylene})_mOH]_{p+q} \qquad \text{VII}$$

where R, 'alkylene', m, p and q have the meanings given above and is reacted with an acid $L(CH_2)_n\,COOH$ where n is an integer of value 1 to 5 and L is a halogen, or a chloride or anhydride thereof, there is produced an intermediate halo compound of the general formula

$$\left[R\right] \begin{array}{l} [(\text{O-alkylene})_m\ OH]_q \\ [(\text{O-alkylene})_m\ O\ CO(CH_2)_n\ L]_p \end{array} \qquad \text{VIII}$$

which reacts with a water soluble thiosulphate to produce a compound of formula I where X presents a $—CO(CH_2)_n—$ residue.

The esterification reaction can conveniently be carried out by refluxing the polyol and the halogenocarboxylic acid in a non-polar organic solvent, for example toluene. A catalyst e.g. toluene-*p*-sulphonic acid is normally present and the water produced is distilled off and collected in a Dean and Stark trap. The halo-ester so obtained can be converted to the Bunte salt by reaction with sodium thiosulphate in an aqueous/alcoholic medium under reflux.

More specifically, a compound of the formula

$$\begin{array}{l} CH_2—(\text{O-alkylene})_m\ OH \\ | \\ CH\ —(\text{O-alkylene})_m\ OH \\ | \\ CH_2—(\text{O-alkylene})_n\ OH \end{array}$$

esterified with the haloacid $L\ (CH_2)_n\ COOH$ where L is halogen, or an anhydride or chloride thereof yields a product

$$\begin{array}{l} CH_2(\text{O-alkylene})_mOCO(CH_2)_nL \\ | \\ CH(\text{O-alkylene})_mOCO(CH_2)_nL \\ | \\ CH_2(\text{O-alkylene})_mOCO(CH_2)_nL \end{array}$$

which can be further reacted as above.

Compounds according to the invention can also be produced by treatment of the

appropriate thiol compounds with a water-soluble bisulphite and a water-soluble tetrathionate. Suitable thiol compounds have

(a) a radical containing at least one poly (oxyalkylene) chain and at least two chain terminating oxygen atoms notionally derived from terminal hydroxyl groups;

(b) at least two thiol groups each bound through an alkylenecarbonyl group to a chain terminating oxygen atom.

Suitable thiols include those of the general formula

$$[R]\ [(O\text{-alkylene})_m\ O\ CO\ CH_2SH]_{p_1} \qquad IX$$

wherein R, 'alkylene' and m are as defined in formula I and p_1 is an integer from 3 to 6.

The compounds of formula IX can produce Bunte salt terminated compounds of the general formula I on warming with sodium bisulphite and sodium tetrathionate in an aqueous/alcoholic medium. Suitable thiol terminated starting materials are disclosed, for example, in British Patent Specification No. 1,278,934. The reaction may also give rise to compounds containing disulphide linkages, such compounds being of the general formula IV or V. Normally these disulphide compounds which are within the scope of the invention, are minor components of the reaction products.

Curing Reactions

Polymeric compounds containing substantially two or more Bunte Salt groups per molecule are curable and may be converted into insoluble cross-linked condensation products. It has been found that when preparing the compounds by substitution of terminal halo-atoms, substitutions of about 60% give satisfactory curable products. The polymers cure on prolonged exposure to light or heating. Curing is effected by treatment with acids, bases or reducing agents. Suitable reducing agents include quaternary phosphonium compounds, for example THPC (tetrakis(hydroxymethyl) phosphonium chloride), sodium borohydride, thioglycollic acid and thiol containing compounds such as thioethanol, cysteine, thioglycerol and resins containing free thiol groups such, for example, as those mentioned in British Specification No. 1,278,934. Curing may also be assisted by nucleophilic substances such as thiourea, nitrous acid, acid hypochlorite, iodide ions or thiocyanate ions. Diamines, such as ethylene diamine, diethylene triamine 1,6 diaminohexane and piperazine, are valuable curing agents by the reaction

$$2\ [—OCOCH_2\ SSO_3—Na^+] + H_2NRNH_2 \rightarrow —OCOCSNHRNHCSCOO—$$

In addition tertiary amines may promote curing

The compounds of this invention may be insolubilised by treatment with polyvalent metal ions, for example magnesium ions, and it may be advantageous to treat the compounds in this way and simultaneously or subsequently treat them with a curing agent.

Textile Applications

Textile material can be treated by applying thereto a curable compound according to this invention and curing the polymer on the material. The compound may be of any of the general formulae I to VI and from 0.1 to 15% of the polymer, preferably 0.5—5% by weight on the weight of material can conveniently be applied.

The compounds may be applied to synthetic fibres, for example polyamide, polyester or acrylic fibres and impart an attractive handle thereto. In addition they may also act as antistatic agents. They are useful pigment binding agents on all fibres both natural and synthetic. The compound may be applied to natural or regenerated cellulosic fibres and can impart wrinkle resist and permanent press properties thereto.

The compounds are of especial value for the treatment of keratinous textile materials, usually derived from the wool of sheep, or from alpaca, cashmere, mohair, vicuna, guanaco, camel hair or llama or blends of these materials with sheep's wool. The treatment of such materials according to the invention can be used to impart shrink-resist and/or permanent press properties thereto. The wool may be mixed with other textile fibres, for example polyamide, polyester or cellulosic fibres but in the shrink-resist treatment of wool-containing fabrics generally at least 30% of the material is wool, and wool rich blends, for example 60:40 wool/cotton blends, 80/20 wool/nylon blends and 80:20 wool/polyester blends may be used.

The polymeric compounds of this invention may be applied to the textile material by any conventional technique, for example by padding or by exhaustion from a dyebath. In the treatment of wool the polymers have the advantage that they are anionic and are compatible with wool dyes which normally contain anionic solubilising groups. Thus acid levelling, acid milling, premetallised and solubilised vat dyes can be used but for best dye fastness to washing it is preferred to use fibre-reactive dyes, i.e. dyes that can react with the keratin fibre and become covalently bonded thereto. The acid levelling dyestuffs can be, for example, of the azo type and should be water soluble and contain at least one anionic solubilising group, generally a sulphonic acid group. Acid milling dyes generally have a greater molecular weight and fewer solubilising groups than the acid levelling dyes, but there is no rigid distinction between the two classes. The premetallised dyes comprise a class of dyes having *o,o'*-dihydroxy azo, *o*-amino-*o'*-hydroxy azo or *o*-carboxyl-*o'*-hydroxy azo groups which are co-ordinated to a metal atom, for example chromium or cobalt. The dyes may be used as 1:1 or 2:1 complexes. Vat dyes, which are most commonly of the indigoid or anthraquinone structure, are solubilised by conversion to their water-soluble leuco esters and can subsequently be developed after application by oxidation to the insoluble form. It has also been found that pigments can be applied to wool fibres by pad-dyeing or printing, with good wash and rub fastness, in the presence of a curable compound according to this invention.

The process is especially advantageous when combined with dyeing with an aqueous solution of a wool dye. Previous shrinkproofing resins have been found to be incompatible with reactive dyes owing either to the formation of ion complexes or to their water insolubility. A preferred process for dyeing with such a dye comprises impregnating the fibres at a pH of 5—12, e.g. by padding, with an aqueous composition comprising a reactive dye and a water soluble polymer according to this invention, a reducing agent for the keratin and an additive for facilitating penetration of the dye into the keratin fibres, storing the dyed and polymer-treated fibres in the presence of moisture to allow penetration of the dye into the fibres and deposition of the resin thereon, and thereafter subjecting the fibres to a washing treatment. If necessary the washing solution may contain 0.1—2.0% by weight of a curing agent for the resin. When producing shades on wool or similar materials by a method of impregnation followed by storage, it is accepted practice to add to the dye liquor a surfactant which produces rapid wetting of the wool at room temperature. These additions are exemplified by non-ionic condensation products of e.g. lauryldiethanolamide. The anionic Bunte Salts can themselves serve as wetting agents.

The reactive dyes which may be employed also include whitening agents which react with fibres in the same way. Dyestuffs falling within this class can incorporate the following groups:

epoxy-, ethylene-imino-, isocyanate, isothiocyanate, carbamic acid aryl-ester-, propiolic acid amide, monochloro- and dichloro-crotonylamino, chloro-acrylamino-, thiosulphato, labile halo atoms, trichloro-pyridazino-, dichloroquinoxalino-, allylsulphonyl-, monochlorotrizinyl-, vinylsulphonyl-, and certain reactive ammonium or hydrazinium residues.

Especially good results in pad-dyeing are obtained with highly reactive dyes, for example those incorporating a 2,4 dichlorotriazinyl, 2,3 dichloroquinoxalino, 2-chloro-4 methoxytriazinyl, 2,4 dichloro-5-carbonyl-pyrimidine or 2,4-difluoro-5-chloro-pyrimidine group.

Reducing agents are preferably incorporated into the pad liquor, and examples include alkali metal, ammonium and amine sulphites and bisulphites, for example, sodium bisulphite, sodium metabisulphite and monoethanolamine bisulphite, certain quaternary phosphonium compounds, for example, tetrakis-(hydroxymethyl)-phosphonium chloride, sodium borohydride, and thioglycollic acid and other materials capable of breaking disulphide bonds in the keratin molecule. The amount of reducing agent per 100 parts by weight of paste may for example be from 1 to 50, preferably from 1 to 20 parts by weight. Sodium bisulphite is preferred and has the advantage that it exerts a bleaching action on the wool and therefore allows very bright shades to be obtained, and also appears to promote reaction between the wool and the polymer.

It is preferred to include an additive in the pad liquor to assist penetration of the dye into the keratin fibres. While the invention does not depend on any theory as to its mode of action, it is believed that the additive can cause swelling of the keratin fibre and/or disaggregation of the dyestuff. Suitable additives include acid amides or

thioamides, for example urea, thiourea, sulphamide, or derivatives thereof, furfuraldehyde and cinnamaldehyde, and the additive is preferably present in the aqueous composition in a concentration of 100—400 grams per litre, especially in the case of urea about 300 g/l.

The simultaneous dyeing and resin treatment can be carried out by dissolving the reactive dye and the polymer in water, preferably in the presence of an acid amide or thioamide, for example, urea, and in the presence of a reducing agent for the keratin, for example sodium bisulphite, and subsequently impregnating the fibres with the dye composition, for example, by impregnation with a pad mangle. The process can be carried out at ambient temperatures or from 10 to 60° C. although slightly elevated temperatures, preferably below 50° C. are best. Generally speaking, temperatures in the range 10 to 60° C. are suitable. The dyeing can be carried out at a pH in the range 2—12 but is preferably conducted at a pH of about 10. The fibres are allowed to remain in contact with the dye for the minimum time for proper penetration, e.g. between 10 min. and 72 hrs, typically between 1 and 24 hrs. For example, the fibres may be removed, squeezed to express excess liquid and then stored in the presence of moisture for 10 mins. to 72 hrs. to ensure that the bulk of polymer and of the dye becomes attached to the keratinous fibres leading ao a full shade development of the dye. After the storage period the fibres are normally washed off with a solution of a curing agent, for example a mixture of magnesium chloride and ammonium thioglycollate and optionally are subsequently treated with an aqueous solution of a base. Conventional equipment can be used for applying these solutions, for example, a beam washer, a winch or a conventional washing range.

Pigment Dyeing

The polymers of the invention can be used to advantage in the production of fast dyed shades on all fibres using pigments. Pigments are generally classified as water insoluble colours and their current use on textile materials is limited by the following restrictions:

i) Pale depths only can be achieved due to the poor rub fastness of deeper shades.
ii) A pigment dyeing or print always appears 'glassy' to the trained observer.
iii) Usually up to 10% o.w.f. polymer binder is employed which has a very great effect on harshening the 'handle' of the material.

The use of the Bunte Salt polymers either alone or in a mixture completely eliminates the above problems and allows the production of a wide range of satisfactory shades on all fibres by printing or dyeing. Printing or dyeing is carried out with a mixture of the Bunte Salt polymer, pigment and thickener followed by a curing step which may be a simple cold rinse in a solution of reducing agent or diamine, or which may be a heat curing step carried out for example for 5 minutes at 140° C. Washing in cold water completes these processes.

One great advantage of the pigment dyeing procedure is that solid shades can be achieved on wool/synthetic fibre blends. Other advantages include the shrink proofing effect imparted to wool and the antistatic effects and wrinkle resistance imparted to such fibres as polyester cotton.

Treatment of Hair

It has been found that the polymeric compounds of the invention can be employed for the treatment of hair including human hair.

They can be formulated into a composition for the treatment of hair comprising the polymeric compound and at least one inert solvent or diluent. Such composition contains from 0.5 to 15% by weight, preferably from 2 to 6% by weight, of the polymeric compound. The composition preferably also contains a reducing agent for the keratin (other than a curing agent for the polymer), for example sodium bisulphite, and optionally also a nucleophilic substance such as thiourea. The reducing agent is conveniently present in an amount of from 0.2 to 10% by weight based on the weight of the composition. In order that the composition should have satisfactory storage stability it preferably contains at least 20% by weight of water and is adjusted to pH in the range 3—10, preferably about 7.

The composition may be in the form of an aqueous or aqueous/alcoholic solution and may be, for example, in the form of a shampoo or wave-setting lotion. It may alternatively be in the form of a cream or gel, the polymer being dissolved in the aqueous phase thereof. The composition may contain any other conventional ingred-

ient for use in cosmetics provided that the ingredient does not react with Bunte Salts. For example the composition may additionally contain one or more surfactants, hair dyes, pigments, perfumes, swelling agents or thickening agents. The composition may also be formulated as an aerosol.

The polymeric compounds when applied to hair can enhance its appearance by making it brighter and may also facilitate combing out of the hair. When the hair has become degraded by the action of, for example, sea water, sunlight, bleaching agents or permanent waving agents, the compounds may have the effect of increasing the strength thereof. The compounds may also be used for the shape stabilisation of hair and are therefore of value for incorporation into permanent waving compositions. The hair may be formed into the desired shape or configuration, a solution of the polymer is applied thereto and the polymer is subsequently cured.

The compounds can be applied to the hair by any conventional method, for example by brushing, spraying or dipping, and preferably remain in contact with the hair for a period of 5—30 minutes. The hair is then rinsed with an aqueous solution of a curing agent, for example a mixture of ammonium thioglycollate and magnesium chloride.

The invention is illustrated by the following Examples of the preparation of compounds according to the invention. Examples of their application to fibres or filamentary materials are given in our Application No. 57313/71 (Serial No. 1,423,341).

EXAMPLE I.

A polythiol was prepared from a mixture of 800 g (0.2 g-mol) of a triol of average molecular weight 4,000 made from glycerol and propylene oxide, 55.2 g (0.6 g-mol.) of thioglycollic acid, 5 g of toluene-*p*- sulphonic acid and 350 ml of toluene by heating to reflux with stirring in an atmosphere of nitrogen. Water (10.8 ml, 0.6 g-mol.) formed during the reaction was removed as its azetrope with toluene. The mixture was cooled and washed with water, and the organic layer was separated. On removal under vacuum of the solvent from the organic layer there remained 793 g (94% of the theoretical yield) of the desired tris(thioglycollate) having a thiol content of 0.59 equiv./kg.

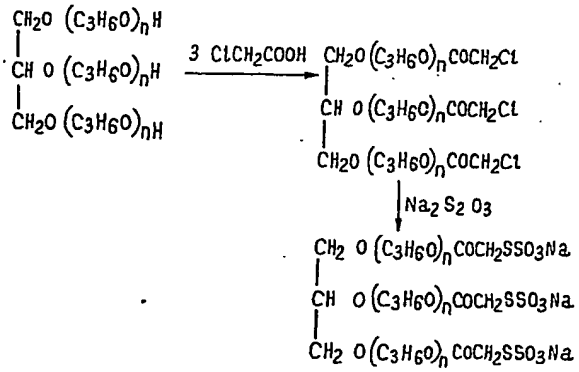
The above polythiol resin (1 mole) was treated with sodium bisulphite (4 moles) in water and isopropanol was added to the liquor until a clear solution was obtained. The solution was heated to 60° C. for 4 hours and sodium tetrathionate ($Na_2S_4O_6$, 2 moles) was added, the solution then being maintained at 60° C. for a further hour. A further 4 moles of sodium bisulphite and 2 moles sodium tetrathionate were then added as before. A yellow oil separated from the solution and was discarded. The solution was cooled and allowed to stand overnight, and the solvent was evaporated off in vacuo to give a clear, viscous, curable, organic polymer which was soluble in water and exhibited surface active properties, and the infrared spectrum of the product showed bands characteristic of Bunte Salt groups at 1030 cm^{-1} and 1050—1190 cm^{-1}. The product was anionic and readily precipitated when treated with the blue basic dye Basacryl Blue XRL. White precipitates of cured resin formed readily on treatment with hydrochloric or sulphuric acid, magnesium chloride, THPC or ammonium thio-

glycollate, and at pH 2.0 with thioglycollic acid in the presence of tertiary amines or thiourea. Boiling in dilute mineral acids produced the corresponding insoluble thiols, but disulphides can be formed under these conditions if thiourea is present.

EXAMPLE II.

A triol (100g) of average molecular weight 3,000 prepared by condensation of glycerol with propylene oxide (Polyurax G3000, B.P. Chemicals Ltd.) was dissolved in toluene (300 ml). Chloroacetic acid (15 g) was added together with toluene *p*-sulphonic acid (5 g). The mixture was refluxed for 4 hours at 110° C. in an atmosphere of nitrogen and the water liberated was collected as its azeotrope with toluene in a Dean and Stark apparatus. The theoretical yield of water (1.8 ml) was recovered. The reaction mixture was washed with water and sodium bicarbonate (1% w/v) several times to remove excess chloracetic acid and catalyst, and the toluene was removed by rotary vacuum evaporation. The residual tris-chloroacetyl ester (95 g) was dissolved in isopropanol (300 ml) and sodium thiosulphate pentahydrate (30 g) in water (50 ml) was added. Isopropanol and water were subsequently added as required to maintain a clear solution, together with acetic acid to bring the pH to 5.0. Refluxing was carried out for 4 hours at 80° C. with stirring and at the end of this time a sample of the reaction liquor dissolved in water without turbidity. The solution was cooled and allowed to stand for 10 hours after which it was observed that separation into two phases had occurred. The upper resin phase was separated from the lower aqueous phase which contained a high proportion of dissolved salt. The resin phase was evaporated down *in vacuo* to give a clear viscous resinous material (92 g) which was readily soluble in water and exhibited surface active properties. The infra-red spectrum exhibited bands of 1030 and 1050—1190 cm^{-1} characteristic of Bunte Salt groups. Estimation of the Bunte Salt groups by conversion to thiol groups and subsequent titration indicated the presence of three Bunte Salt groups per molecule.

The reaction is believed to take place as follows:



In like manner Bunte Salt polymers were prepared from the following polyol starting materials:—Propylan G 1000, G 1500, G 3000, G 4000 and G 5000 (Lancro Chemicals Ltd) and Voranol CP 700 (Dow Chemical Co), the figures indicating the molecular weight of the polyol. The word VORANOL is a Trade Mark.

EXAMPLE III.

The polymer prepared in Example II decomposed over the course of a few days when allowed to stand. A composition which could be stored for prolonged periods was prepared by diluting the evaporated product with water until the solids content was 80%, and adding a buffer (disodium hydrogen phosphate) to maintain the pH at about 7. The resulting concentrated solution was stored for a period of several months without noticeable deterioration.

EXAMPLE IV.

Propylan 3 (300g), glycerol/propylene oxide condensation product of molecular weight 3000, was dissolved in toluene (300 ml) and β-chloropropionic acid (80 g) and toluene *p*-sulphonic acid (15 g) were added. The mixture was refluxed for 5 hours at 110° C. and the expected 5.4 ml of water was distilled off and collected as its

azetrope with toluene in a Dean and Stark trap. The mixture was cooled, washed with aqueous sodium bicarbonate and the resulting tris (β-chloropropionyl) ester was recovered by evaporation. A portion of the ester (200 g) was dissolved in ethanol (200 ml) and potassium iodide (12 g) was added. The mixture was refluxed for 1 hour after which a precipitate of sodium chloride was noted, the product now being in the form of the tris (β-iodopropionyl ester). Sodium thiosulphate pentahydrate (70 g) in water (100 ml) was added and the mixture was refluxed for 6 hours. At the end of this time a sample of the mixture when added to water was completely miscible and no turbidity appeared. The mixture was cooled and allowed to stand overnight. It separated into two phases of which the upper phase contained a pale yellow curable resin which was readily soluble in water, exhibited surface active properties, and gave an immediate precipitate with THPC. The product is believed to be

$$\begin{array}{l} CH_2\ O(C_3H_6O)_n\text{—}CO\ CH_2\ CH_2\ SSO_3Na \\ | \\ CH\ O(C_3H_6O)_n\text{—}CO\ CH_2\ CH_2\ SSO_3Na \\ | \\ CH_2\ O(C_3H_6O)_n\text{—}CO\ CH_2\ CH_2\ SSO_3Na \end{array}$$

The remaining ester portion was similarly treated, but without iodide catalysis; no Bunte Salt was formed.

EXAMPLE V.

A diol of molecular weight approximately 2,000 containing propylene oxide derived units (Propylan D 2112 Lankro Chemicals Ltd.) (212 g.) was dissolved in toluene (150 ml) and chloracetic acid (50 g) and toluene-*p*-sulphonic acid (12 g) were added. The mixture was refluxed for 1 hour at 125° C. and cooled. The excess acid was removed by stirring with sodium carbonate (30 g) in water (500 ml) for 1 hour. The organic layer was separated and the dissolved ester was recovered by evaporation.

The ester was dissolved in isopropyl alcohol (200 ml) and sodium thiosulphate pentahydrate (170 g) in water (150 ml) was added. The mixture was refluxed for 2 hours, cooled and allowed to stand. Separation into 2 phases occurred, and the upper resin-containing phase was separated and concentrated as described in Example I. A water-soluble resin was obtained which exhibited surface active properties and gave an immediate precipitate with THPC. The infra-red spectrum of the product showed bands characteristic of Bunte Salt groups.

WHAT WE CLAIM IS: —

1. A curable polymeric compound containing as least one poly (oxyalkylene) chain and substantially two or more thiosulphuric acid or thiosulphate groups each such group being bound through an organic acyl group to a terminating oxygen atom of a poly (oxyalkylene) chain.

2. A polymeric compound according to Claim 1 comprising:

(a) the polyvalent residue of a polyhydric alcohol;
(b) bound to this residue at least two poly (oxyalkylene) chains;
(c) at least two thiosulphuric acid or thiosulphate groups each bound through a respective alkylenecarbonyl group to a chain terminating oxygen atom.

3. A compound according to Claim 1 or 2 having substantially three thiosulphuric acid or thiosulphate groups per molecule.

4. A compound according to any preceding claim having a molecular weight of 500—10,000.

5. A compound according to any preceding claim having the general formula

$$\left[R\right] \begin{array}{l} [(O\text{-alkylene})_m\ OH]_q \\ [(O\text{-alkylene})_m\ O\text{—}CO(CH_2)_n\text{—}SSO_3Y]_p \end{array}$$

wherein

p is an integer from 2 to 6;

q is such that (p+q) is from 2 to 6;

m is an integer of at least 2 and may have different values in each of the p and q chains;

n is an integer of from 1 to 5;

R represents a radical formed by removal of the hydroxyl groups from an aliphatic polyhydric alcohol containing at least two carbon atoms; each 'alkylene' group contains a chain of 2 to 6 carbon atoms between consecutive oxygen atoms;

Y represents a hydrogen atom or a salt forming ion or group.

6. A compound according to any preceding claim of the general formula

$$R\,[(O\text{-alkylene})_m\,O{-}{-}CO(CH_2)_n{-}{-}SSO_3Y)_{p_1}$$

wherein m, X and Y and 'alkylene' are as defined in Claim 5. R represents a radical derived from an aliphatic alcohol containing 3—6 carbon atoms and 3—6 hydroxyl groups and p_1 is an integer from 3 to 6.

7. A compound according to Claim 5 or 6 where R represents the residue of an alcohol containing 3—6 carbon atoms and 3 hydroxyl groups.

8. A compound according to any one of Claims 5 to 7 wherein R represents a residue derived from glycerol.

9. A compound according to any one of Claims 5 to 8 wherein the alkylene groups comprise propylene groups or a mixture of ethylene and propylene groups.

10. A compound according to any preceding claim in the form of its sodium or potassium salt.

11. A compound according to any preceding claim of the general formula

$$\begin{array}{l} CH_2{-}(O\text{-alkylene})_m\ O\ CO\ CH_2\ SSO_3H \\ | \\ CH{-}(O\text{-alkylene})_m\ O\ CO\ CH_2\ SSO_3H \\ | \\ CH_2{-}(O\text{-alkylene})_m\ O\ CO\ CH_2\ SSO_3H \end{array}$$

where m has the same meaning as in Claim 5 and their alkali metal, ammonium or amine salts.

12. A polymeric compound according to Claim 1 substantially as hereinbefore described.

13. A process for preparing a curable polymeric compound according to Claim 1 which comprises esterifying an alcohol containing at least one poly (oxyalkylene) chain and at least two terminal hydroxyl groups with a halogen substituted carboxylic acid or functional derivative thereof and reacting the resulting halogeno-ester with a water-soluble thiosulphate.

14. A process according to Claim 13 which comprises refluxing an alcohol of the general formula

$$R\,[(O\text{-alkylene})_m\,OH]_{(p+q)}$$

with a halogen-substituted acid of the general formula $L(CH_2)_nCOOH$ (where L is halogen) in a non-polar organic solvent to produce a compound of the formula

$$\begin{array}{ll} [R] & [(O\text{-alkylene})_m\,OH]_q \\ & [(O\text{-alkylene})_m\,O\,CO(CH_2)_n\,L)_p \end{array}$$

and subsequently reacting this halogen-containing compound in an aqueous alcoholic medium with a water soluble thiosulphate; the symbols R, 'alkylene', p, q, m and n having the same meaning as in Claim 5.

15. A process according to Claim 13 which comprises esterifying a compound of formula

$$\begin{array}{l} CH_2{-}(O\text{-alkylene})_m\,OH \\ | \\ CH{-}(O\text{-alkylene})_m\,OH \\ | \\ CH_2{-}(O\text{-alkylene})_m\,OH \end{array}$$

with the halogen-substituted acid or an anhydride or chloride thereof to yield a product of formula

$$\begin{array}{l} CH_2(O\text{-alkylene})_mOCO(CH_2)_nL \\ | \\ CH(O\text{-alkylene})_mOCO(CH_2)_nL \\ | \\ CH_2(O\text{-alkylene})_mOCO(CH_2)_nL \end{array}$$

and subsequently reacting this halogen-containing compound with a water soluble thiosulphate; the symbols m, n and 'alkylene' having the same meaning as in Claim 5.

16. A process according to Claim 14 or 15 wherein the acid is chloroacetic acid.

17. A process for preparing a curable polymeric compound as defined in Claim 1 which comprises reacting with a water soluble bisulphite and a water soluble tetrathionate, a compound containing

(a) a residue including at least one poly (oxyalkylene) chain and at least two chain terminating oxygen atoms notionally derived from terminal hydroxyl groups;

(b) at least two thiol groups each bound through a respective alkenecarbonyl group to a terminating oxygen atom of a poly (oxyalkylene) chain.

18. A process according to Claim 17 which comprises reacting a thiol of the formula

$$[R]\ [(O\text{-alkylene})_m\ O\ CO\ CH_2\ SH]_{p_1}$$

with a water soluble bisulphite and a water soluble tetrathionate; the symbols R, 'alkylene' and m having the same meaning as in Claim 5 and p_1 being an integer from 3 to 6.

19. A process according to Claim 17 or 18 wherein the thiol is of formula

$$\begin{array}{l} CH_2\ (O\ C_3\ H_6)_m\ O\ CO\ CH_2\ SH \\ | \\ CH\ (O\ C_3\ H_6)_m\ O\ CO\ CH_2\ SH \\ | \\ CH_2\ (O\ C_3\ H_6)_m\ O\ CO\ CH_2\ SH \end{array}$$

20. A process for preparing a polymeric compound according to Claim 1 substantially as described in Example I herein.

21. A process for preparing a polymeric compound according to Claim 1 substantially as described in Example II herein.

22. A process for preparing a polymeric compound according to Claim 1 substantially as described in Example III herein.

23. A process for preparing a polymeric compound according to Claim 1 substantially as described in Example IV herein.

24. A process for preparing a polymeric compound according to Claim 1 substantially as described in Example V herein.

25. Polymeric compounds produced by the process of any one of Claims 13 to 24.

26. The cured polymeric product of a curable compound according to any one of Claims 1 to 12 or 25.

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